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Synthesis and Solution Properties of Poly[*N*,*N'*-(*p*-phenylene)-3,3',4,4'-biphenyltetracarboxylic acid diamide]

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ABSTRACT: The polyimide poly[*N*,*N'*-(*p*-phenylene)-3,3',4,4'-biphenyltetracarboxylic acid diimide] (BPDA-PDA) is used as a dielectric material in the electronics industry. Although the imidized polymer is insoluble in any organic solvent, the precursor polyamic acid is soluble in amide-type solvents or dimethyl sulfoxide (DMSO). A series of 10 polymers from the polycondensation of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride (BPDA) and *p*-phenylenediamine (PDA) with $4800 < M_w < 75\,000$ have been synthesized by controlling the stoichiometry. The solution properties were investigated in NMP (*N*-methylpyrrolidinone) and DMSO by using low-angle light scattering, viscometry, and size exclusion chromatography with a light scattering detector. Estimates of the molecular flexibility from the dilute solution properties are compared with those calculated based on a freely rotating model.

Introduction

The group of polymers containing the imide moiety in the polymer backbone are known as polyimides. In most applications, an initial high molecular weight polymer is formed by the condensation of a dianhydride with a diamine to a poly(amic acid). In this soluble form, films may be cast, and then the final imidization (or "cure") is accomplished thermally with elimination of water (Figure 1). In this study, we have focused on the poly(amic acid) prepared by the condensation of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride (BPDA) with *p*-phenylenediamine (PDA). The combination of low thermal expansion coefficient (TEC) with the high modulus in these materials makes them candidates for many uses in the microelectronics industry.[1-7] The advantages of a low-TEC material such as BPDA-PDA over the conventionally used PMDA-ODA-based polyimides are the higher density, low thermal expansion coefficient (matching that of silicon), tensile strength and Young's modulus (about 3 times that of conventional PMDA-ODA), high thermal decomposition temperature, slightly lower dielectric constant, and low absorbed moisture content. The final imidized polymer of BPDA-PDA is not soluble in any known solvent, so that information about its molecular properties must be obtained from the precursor amic acid form. The initial polycondensation to produce the polyamic acid essentially determines both the average molecular weight (degree of polymerization) and the distribution of molecular weight of the final polyimide. A series of these amic acid BPDA-PDA polymers with varying molecular weight has been prepared, and the dilute solution behavior of these polymers in dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidinone (NMP) has been examined by low-angle light scattering (LALS), viscometry (η), and size exclusion chromatography coupled with a multiangle light scattering detector (SEC-LS).

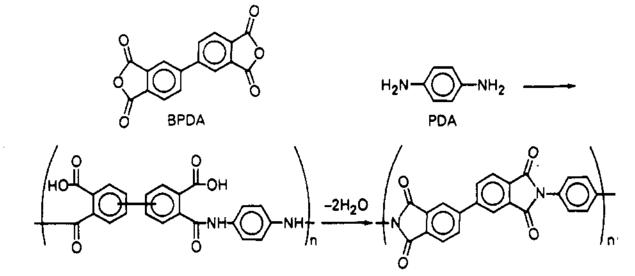

Figure 1. Synthesis of BPDA–PDA amic acid and final polyimide.

Comparisons of this work on BPDA-PDA can be made with earlier work on the more widely used poly(amic acid) PMDA-ODA, based on pyromellitic dianhydride (PMDA) and oxydianiline (ODA). Molecular weight control of PMDA-ODA poly(amic acids) has been shown to be governed by classical step growth behavior when careful control of monomer purity, anhydrous solvents, and the absence of atmospheric moisture are used.[8] Both light scattering and viscometry measurements demonstrate unusual polyelectrolyte effects in dilute NMP solutions of PMDA-ODA that can be eliminated by careful redistillation of this solvent.[9,10] The molecular parameters determined by light scattering and viscometry show some variation with the solvents used.[9,11,12]

Experimental Section

NMP (Aldrich, HPLC grade) was purified by distillation at reduced pressure from P_2O_5. DMSO (EM Science) was distilled from calcium hydride at reduced pressure. 3,3',4,4'-Biphenyltetracarboxylic acid dianhydride (BPDA) was purchased from Chriskev Co., Inc., and was used as received. PDA (Aldrich) was distilled under argon from $ZnCl_2$ into a tared reaction vessel immediately before the polymerization.

The polyamic acids were synthesized as follows: Solid BPDA was added slowly to a mechanically stirred 5% solution of PDA under argon. The internal temperature was maintained at 5 °C or less with an ice/acetone bath. The BPDA was then washed in with the additional solvent needed to bring the polymer concentration to 10%. The solutions were allowed to stir overnight at room temperature and were then stored under refrigeration.

Polymers with various molecular weights were obtained by varying the proportion of reactants in the feed with the diamine as the reactant in excess. Number average molecular weights were predicted according to classical step growth behavior. The number average degree of polymerization, $\bar{X}_n$, was calculated by using

$$\bar{X}_n = \frac{1+r}{1-r} \qquad (1)$$

where r is the ratio of the total number of anhydride function-

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Table I
Molecular Parameters for BPDA-PDA Polyamic Acids

sample	solvt	r	$\bar{M}_w$(calc)	$\bar{M}_w^{LS}$	$[\eta]$, mL/g	$10^4A_2^{LS}$, mL/g·dlt
1	DMSO	0.8510	4300	4800	30.5	34
2	DMSO	0.8510	4300	7200	26.6	32.2
3	DMSO	0.9226	9300	8300	42	27
4	DMSO	0.9606	19000	16800	62.8	28
5	DMSO	0.9773	33000	22000	71.9	24
6	DMSO	1.0000	∞	56400	185	19.6
7	NMP	0.8510	4300	5900	25.7	28
8	NMP	0.9226	9300	9900	38	24
9	NMP	0.9606	19000	18800	68	22
10	NMP	1.0000	∞	75000	251	15

alities over the total number of excess amine functionalities. The number average molecular weight, $\bar{M}_n$, is defined as

$$\bar{M}_n = \bar{X}_n M_0 \tag{2}$$

where M_0 is the mean of the molecular weights of the two monomers. For BPDA-PDA, M_0 is 201.2.

The differential refractive index increment, dn/dc, was measured by using a Chromatix laser differential refractometer, at 25 °C and 632.8 nm. In NMP, dn/dc varied slightly from 0.22 to 0.23 depending on the purity of the solvent. The dn/dc in DMSO was 0.209.

Intrinsic viscosity, $[\eta]$, measurements were made at 25 °C using an Ubbelohde suspended level capillary viscometer equipped with an automatic viscosity timer (Wescan). All solutions were filtered through 0.5-μm Fluoropore (Millipore Corp.) filters before measurement. Measurements of the relative and specific viscosities, η_{rel} and η_{sp}, were obtained at four to five concentrations, and values for the $[\eta]$ were determined by extrapolation of the reduced and inherent viscosities to infinite dilution according to the Huggins and Kraemer relations

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + k''[\eta]^3c^2 + \cdots \tag{3a}$$

or

$$\ln \eta_{rel}/c = [\eta] - (^1/_2 - k')[\eta]^2c + (^1/_3 - k' + k'')[\eta]^3c^2 + \cdots \tag{3b}$$

where η_{sp}/c is the reduced viscosity and $\ln \eta_{rel}/c$ is the inherent viscosity. Linear plots were obtained except where polyelectrolyte effects were observed.

Low-angle light scattering (LALS) measurements were made using a Chromatix KMX-6 (LDC Milton Roy) light scattering photometer. This instrument measures light (632.8 nm) scattered in a solid angle (~4°) about the incident beam. Measurements of the Rayleigh factor, R_θ, were obtained for four to five concentrations (1 mg/mL < c < 20 mg/mL), and the weight average molecular weight (M_w) was obtained through the relations

$$Kc/R_\theta = M_w^{-1} + 2A_2c + 3A_3c^2 + \cdots \tag{4a}$$

or

$$\sqrt{Kc/R_\theta} = 1/\sqrt{M_w} + A_2c\sqrt{M_w} \tag{4b}$$

which are strictly valid only at $\theta = 0°$ and are used here with $\theta = {\sim}4°$. A_2 is the second virial coefficient, and c is the concentration. Equation 4b is obtained from eq 4a by truncating after the third term and making the substitution $A_3 = {}^1/_3A_2{}^2M$. All solutions for LALS were clarified by filtration through 0.5-μm Fluoropore filters. Use of the square-root plot above yielded linear extrapolations except where polyelectrolyte effects were observed, as discussed below.

The optical anisotropy, δ, was determined for a low-M sample by measuring the polarized (V_V) and depolarized (H_V) components of the scattered light at $\theta = 4°$:

$$H_V/V_V = 3\delta^2/(5 + 4\delta^2) \tag{5}$$

δ^2 was less than 0.01, so corrections for optical anisotropy were negligible. Fluorescence from the solutions was insignificant. Correction for absorption by the colored solutions was made by using the intensity of the transmitted light in calculation of the Rayleigh factor R_θ.

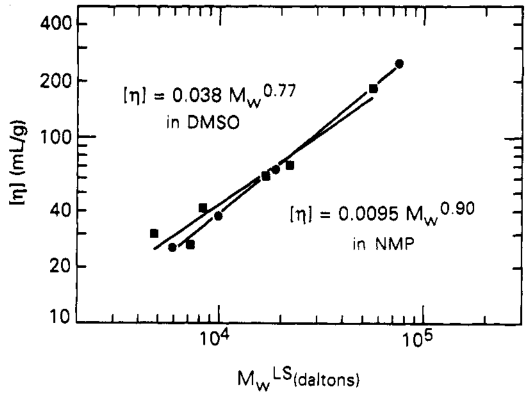

Figure 2. $[\eta]$ as a function of M_w for BPDA-PDA amic acid in DMSO (■) and NMP (●).

Two of the BPDA-PDA samples polymerized in DMSO were investigated by using size exclusion chromatography with a light scattering detector (SEC-LS). A multiangle light scattering detector (DAWN Model F, Wyatt Technology) was used. A Waters liquid chromatograph (GPC I) was used for the separation, consisting of a 590 pump and R401 refractive index detector. Injections were made with a WISP automatic injector. The mobile phase used was NMP, which was stirred over 0.05 M P_2O_5 and filtered through a 1.0-μm Fluoropore filter before use. The columns used were a series of 10^6-, 10^5-, 10^4-, and 10^3-Å nominal porosity cross-linked polystyrene (10-μm particle size, Polymer Laboratories) and were housed in an oven maintained at 60 °C. A more detailed investigation of SEC-LS of polymers of this type was reported previously.[13] For the BPDA-PDA polymers, the 10% polymerization solution in DMSO was diluted to ~4 mg/mL in NMP, and injections of 250 μL were made. With this technique, as many as 13 chromatograms are obtained for each sample, the usual concentration (refractive index or UV–vis absorption) chromatogram plus light scattering chromatograms at each of 12 scattering angles. In principle, both the root-mean square radius of gyration (R_G) and the molecular weight may be obtained at each point on the chromatogram. For the BPDA-PDA polymers, the R_G was too small (<20 nm) to be determined in this manner, and no angular dependence was observed. The molecular weight at a given elution time was calculated as for LS measurements, using the refractive index from the RI chromatogram as a measure of the concentration. For the high dilutions used, the contribution of the second virial coefficient may be ignored. Software from Wyatt Technology was used with an IBM PC-AT to do the calculations. The column set was also calibrated with polystyrene standards, and molecular weight averages relative to polystyrene (M^{PS}) were determined by using software from Nelson Analytical with an IBM PC-XT.

Results

Values of the calculated and experimentally determined (light scattering) weight average molecular weights (M_w(calc) and $M_w{}^{LS}$) are shown in Table I. If a polymerization follows step growth kinetics, the molecular weight distribution can be approximated by a most probable distribution. The polydispersity (M_w/M_n) of a polymer sample derived from stoichiometrically imbalanced monomer ratios is given by

$$M_w/M_n = 1 + pr^{1/2} \tag{6}$$

where p is the extent of the reaction and r is the monomer imbalance ratio.[14] If the reaction of an anhydride with an amine proceeds to completion ($p \rightarrow 1$), then M_w/M_n approaches 2 for small stoichiometric imbalances. Comparison of experimentally determined weight average molecular weights with calculated number average molecular weights suggests the above behavior. An uncertainty of ±10% is expected in experimental molecular weight determinations. The stoichiometric imbalance is

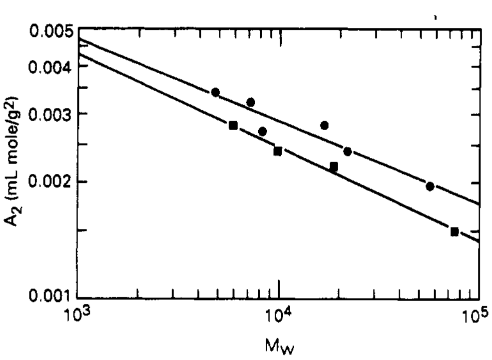

Figure 3. A_2 as a function of M_w for BPDA-PDA amic acid in DMSO (●) and NMP (■).

Table II
SEC-LS Results

sample	M_w^{LALS}	$M_w^{SEC\text{-}LS}$	$(M_w/M_n)^{SEC\text{-}LS}$	M_w^{PS}	$(M_w/M_n)^{PS}$
2	7200	13000	1.05	20900	3.2
6	56400	53700	1.30	93900	2.7

more critical at high molecular weights. Values of p less than 1 will also be most apparent at high M. In practice, values of M_w larger than about 100 000 are rarely achieved for condensation polymerizations. Even very limited side reactions (particularly expected with phenylenediamine) will have a significant effect on the final molecular weight.

Also given in Table I are the second virial coefficients (A_2^{LS}) and the intrinsic viscosities, $[\eta]$, in distilled NMP and DMSO. A log-log plot of $[\eta]$ vs M_w is shown in Figure 2. The data obey the Mark-Houwink relation, $[\eta] = KM^a$, yielding

$$[\eta] = 0.0095(M_w)^{0.90} \tag{7a}$$

$$[\eta] = 0.038(M_w)^{0.77} \tag{7b}$$

in distilled NMP and DMSO, respectively, or

$$[\eta] = 0.020(M_w)^{0.83} \tag{7c}$$

for both sets of data. These relations may be compared with

$$[\eta] = 0.0235(M_w)^{0.735} \tag{8}$$

reported by Miwa and Numata[15] for BPDA-PDA in NMP. $[\eta]$ is in mL/g, and the weight average molecular weight is obtained by light scattering. Equation 8 reported by Miwa and Numata predicts values for $[\eta]$ that are only about one-half those expected from eqs 7 for a given M. As discussed below, eqs 7 are consistent with a model of the polymer that allows essentially free rotation about the rigid segments. Thus, smaller dimensions, as indicated by eq 8 are unlikely.

The molecular weight dependence of A_2 in both NMP and DMSO is shown in Figure 3. While it is clear that A_2 values in both solvents are large, those in DMSO are somewhat larger, indicating a stronger polymer solvent interaction in DMSO. For these samples, $0.5 < A_2M_w/[\eta] < 0.8$, which approaches the upper limit of 0.8-1.2 observed for flexible polymers in good solvents. The molecular weight dependence of A_2 may be expressed as

$$A_2 \propto M^{-\nu} \tag{9}$$

where ν is usually approximately 0.2. Values of ν from Figure 3 are 0.21 and 0.24 for DMSO and NMP, respectively.

Size Exclusion Chromatography. The recently developed technique of SEC-LS provides a direct measure of the molecular weight as the polymer elutes from the column. This eliminates the need for calibration and provides an absolute rather than relative measurement of molecular weight. This is advantageous for the polyimide precursors that can exhibit separation by mechanisms unrelated to molecular size.[13]

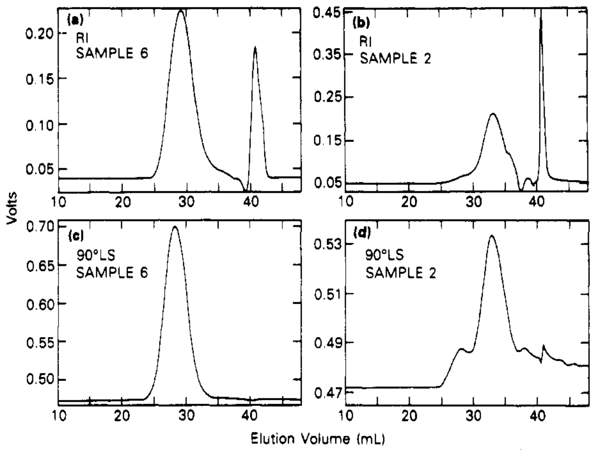

Figure 4. Refractive index and 90° scattering chromatograms for samples 2 and 6.

The SEC-LS results for samples 2 and 6 are listed in Table II. The M_w determined from SEC-LS is in good agreement with M_w from LALS alone for the higher molecular weight sample 6. For the lower M sample 2 the M_w from the SEC-LS is significantly larger than M_w from LS alone. This is due to the low intensity of scattering from the lower M sample. Both the refractive index and 90° scattering chromatograms for samples 2 and 6 are shown in Figure 4. For sample 2, the scattering intensity at the maximum in the chromatogram is only 13% larger than that of the pure solvent. Since the scattering intensity is proportional to M, contributions to the scattering from the low-M portion of the distribution may be insignificant at the high dilutions used for SEC. For sample 2, this results in an erroneously high value for M_w. This effect is also reflected in the values of M_w/M_n determined by SEC-LS. For both samples, M_w/M_n from SEC-LS is significantly less than 2, and for sample 2, it approaches the value of unity expected for a monodisperse polymer. The values of M_w/M_n calculated from the polystyrene calibration are much larger and are more indicative of the distribution. The discrepancy between the values listed (nearly 3) and the expected value of 2 for a most probable distribution may be due to the variety of isomers for this polymer. The estimation of polydispersity from the SEC chromatogram is based on an assumption of a constant proportionality between the hydrodynamic volume and the molecular weight. Clearly, molecules containing larger proportions of the all-para isomer will have larger hydrodynamic volumes and elute earlier than molecules of the same M with larger proportions of meta isomers. Values of M_w/M_n very close to 2 have been observed for similar polymers where the isomers have been separated.[13]

Discussion

Polyelectrolyte Effects in Dilute NMP Solutions. Another similarity between BPDA-PDA and PMDA-ODA amic acid solutions is the anomalous concentration dependence observed in undistilled NMP. Both viscometry and light scattering measurements demonstrate this effect. Viscosities that increase with dilution in as-received (HPLC grade) NMP behave normally when NMP distilled over P_2O_5 is used as the diluent. This is shown in Figure 5 for sample 10, the highest molecular weight sample used in this study.

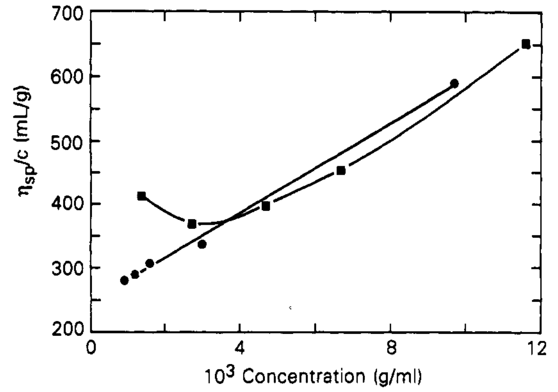

Figure 5. Reduced viscosity as a function of concentration for sample 10: (■) NMP as received; (●) NMP after distillation from P_2O_5.

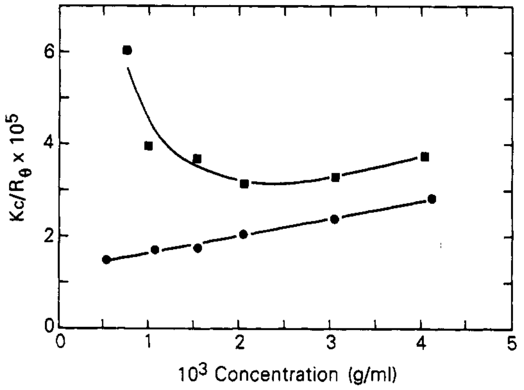

Figure 6. K_c/R_θ as a function of concentration for sample 10: (■) NMP as received; (●) NMP after distillation from P_2O_5.

Light scattering in the as-received NMP also shows unusual effects in very dilute solutions, as shown in Figure 6. The intensity of the light scattered from very dilute solutions is reduced, producing curving plots that cannot be extrapolated in infinite dilution to yield a molecular weight. This behavior, which was observed earlier in PMDA-ODA,[8-11] has been attributed to partial ionization of the polymer induced by amine impurities in the as-received NMP. It is most pronounced in high molecular weight samples, and the light scattering is more sensitive to this effect than viscometry.

Anomalous results have also been observed and reported for size exclusion chromatography of polyamic acids.[16-18] SEC measurements are the most sensitive to partial ionization of the poly(amic acid) due to the very high dilutions used. While addition of a screening electrolyte such as LiBr was found to be successful,[16] results obtained with NMP treated with P_2O_5 were more reproducible.[13]

Molecular Flexibility. The intrinsic viscosity and molecular weight data can also be analyzed by using the analytical expressions of Yamakawa and Fujii for the Kratky–Porod wormlike cylinder,[19,20] as shown in Figure 7. For this model, the intrinsic viscosity may be written as

$$[\eta] = \Phi(L/q)^{3/2}q^3/M \tag{10}$$

where L is the contour length, q is the persistence length, and M is the molecular weight. The friction coefficient, Φ, is a function of L, q, and the hydrodynamic diameter d. Thus, the experimental data may be fit to this expression by adjusting M_L, q, and d. However, a three-parameter fit is not a reasonable approach for the limited data. The hydrodynamic diameter, d, was estimated from the specific volume, V, by using

$$V = \left(\frac{\pi N_A}{4}\right)\left(\frac{d^2}{M_L}\right) \tag{11}$$

The specific volume used was 0.69 mL/g and was estimated by measuring the density of a fully cured and solvent-free film of the polymer. The mass per unit length (M_L, the shift factor), was estimated by M/L, where L is the length of a chain of molecular weight M when fully extended. The persistence length, q, was then determined from the best fit to the experimental data. Use of this model assumes that excluded volume interactions are negligible. Previous work with the amic acid of PMDA-ODA in a reported Θ solvent (NMP/dioxane, 1:3) indicated that excluded volume effects were small ($\alpha_\eta^3 < 1.2$).[9] The increase of the exponent a in the Mark–Houwink relation from its expected value of $^1/_2$ for flexible chains in Θ solvents was shown to be primarily due to inherent short-range correlations (stiffness) rather than long-range excluded volume interactions.[21] For the BPDA-PDA samples, we may estimate α_η using the Yamakawa–Stockmayer expressions for wormlike chains with excluded volume effects.[22] For this crude estimate, we assume $\alpha_\gamma = \alpha_\eta$ and use the rodlike expression for A_2:

$$A_2 = \pi N_A d/(4M_L^2) \tag{12}$$

which is only about 30% larger than the experimental values at the lowest M reported in Table I. For highest molecular weight studied, this estimate yields $\alpha_\eta^3 \sim 1.3$ so that the values for $[\eta]$ at these molecular weights may be as much as 30% higher than would be obtained in a Θ solvent. Figure 7 shows the dependence of $[\eta]$ on M_w for BPDA-PDA in both NMP and DMSO along with the calculated curve for values of q of 2.0, 3.0 and 4.0 nm. Correction of $[\eta]$ at the high molecular weight to reflect the expected excluded volume contribution would not permit a more precise estimate of the persistence length. Values of d, M_L, and q for BPDA-PDA and for several precursors of PMDA-ODA[21] are shown in Table III.

Comparison of the inherent molecular flexibility of various polyimide precursors is best made from an invariant parameter such as the persistence length. For example, although the Mark–Houwink relations are very similar for BPDA-PDA amid acid and the para isomer of

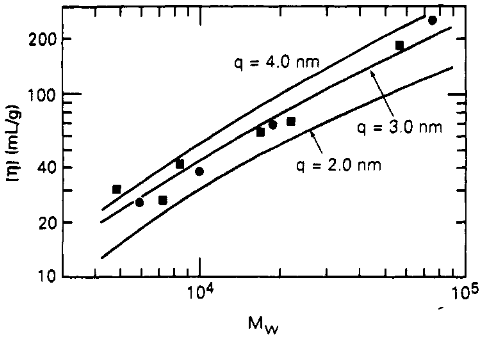

Figure 7. $[\eta]$ as a function of M_w calculated from the Yamakawa–Fujii expressions for the wormlike cylinder with persistence lengths q of 2, 3, and 4 nm. The experimental points are the same as in Figure 2.

Table III
Summary of Wormlike Chain Parameters

polymer	isomer	d, nm	M_L, nm^{-1}	q, nm
BPDA-PDA amic acid	mixed	0.6	245	3.0
PMDA-ODA amic acid	50:50	0.57	250	3.6
PMDA-ODA ethyl ester	meta	0.7	298	1.8
PMDA-ODA ethyl ester	para	0.7	298	4.5

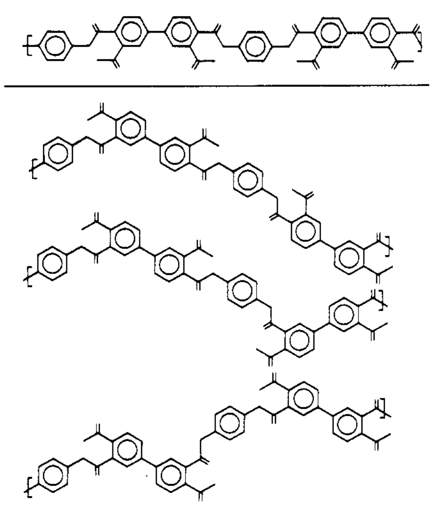

Figure 8. Structural isomers of BPDA-PDA amic acid. Top to bottom: all para; meta-para linked head-to-head; meta-para linked head-to-tail; all meta.

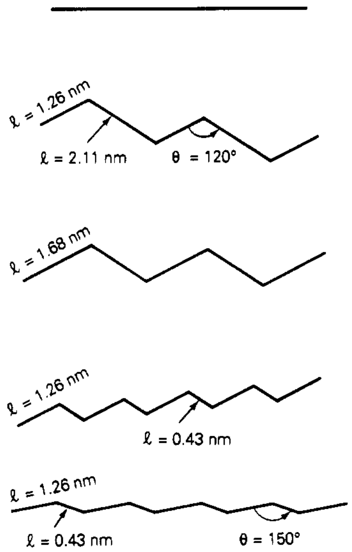

Figure 9. Free rotating models of BPDA-PDA amic acid isomers. Top to bottom: all-para; meta-para linked head-to-head; meta-para linked head-to-tail; all-meta; imidized polymer.

PMDA-ODA ethyl ester,[21] their molecular flexibility is quite different, as evidenced by the values of q in Table III.

Comparison with Models. The experimental estimate for the persistence length, q, may be compared with an estimate predicted from a freely rotating model. This model is the basis for a detailed theoretical prediction of chain dimensions for PMDA-ODA carried out by Birshtein.[23] There are two properties of these polymer chains that contribute to the applicability of the freely rotating model. First, the incorporation of phenyl groups into the polymer backbone produces long backbone "bonds", connected by ether oxygens, about which rotation is essentially free and unhindered by steric constraints.[24] Second, the amide groups in the backbone strongly favor the planar trans configuration (by 5–7 kcal/mol), and so rotation around these bonds contributes little to the overall flexibility.[25] If the only groups present in the backbone are para-linked aromatic rings and amide linkages, then the polymer will be highly extended with a persistence length of 50 nm or more. Such is the case for poly(phenyleneterephthalamide), which is sufficiently extended to form a nematic phase in solution. However, it should be recognized that even such highly extended chains will be random coils at sufficiently high M when in isotropic solutions. The smaller contributions to chain flexibility such as torsional oscillations, non-strict parallelism of the sequential "bonds", or deviations from the flat trans structure of the amide prevent the chain from being a true rigid rod at high M. However, these contributions to flexibility are insignificant relative to the large effect of meta linkages or catenation angles less than 180°. In the case of PMDA-ODA, the chain may be modelled as long rigid "bonds" of length l connected by ether oxygens at valence angles θ about which essentially free rotation occurs.[23] Then the classical Eyring formula

$$r^2 = nl^2\frac{1-\cos\theta}{1+\cos\theta} \tag{13}$$

may be used as an estimate of the mean-square end-to-end distance r^2 for a chain of n effective "bonds". For the BPDA-PDA polymer, estimation of the mean-square end-to-end distance is complicated by the four possible isomers shown in Figure 8. For this polymer, containing no ether linkages, flexibility arises from meta linkages in the backbone. Observation of space-filling models suggests that these meta linkages have little hindrance to rotation so that the freely rotating model may also apply to BPDA-PDA. The all-para isomer (top of Figure 8) contains no meta linkages and is highly extended. The meta-para-linked head-to-head isomer (second structure in Figure 8) may be modeled as a freely rotating chain of alternating "bonds" of length 2.11 and 1.26 nm connected by freely rotating joints at the meta linkages as shown in Figure 9. The meta-para-linked head-to-tail isomer has "bonds" of 1.68 nm, and the all-meta-linked chain has alternating "bonds" of 1.26 and 0.43 nm (see Figure 8). A single BPDA-PDA chain will contain a distribution of these structural isomers. Assuming an equal probability for each isomer, the r^2 of the BPDA-PDA chain may be calculated from

$$r^2 = n_{\mathrm{avg}}l_{\mathrm{avg}}^2\frac{1-\cos\theta}{1+\cos\theta} \tag{14}$$

where θ is the angle of the meta linkage (120°) and l_{avg} is the statistical average length of the "bonds" in the chain. The length of the rigid segment contributed by the all-para isomer is dependent upon how many of these links occur in succession. We estimated l_{avg} assuming all para linkages in a given chain occurred in succession, with the constraint that all four isomers are present with equal probability. For reasonable degrees of polymerization (>30) calculation of l_{avg} converges to $l_{\mathrm{avg}} = 1.6 \pm 0.1$ nm. The persistence length q may be estimated from the infinite molecular weight or flexible chain limit expression for r^2:

$$r^2 = 2Lq \tag{15}$$

The fully extended length L is less than $n_{\mathrm{avg}}l_{\mathrm{avg}}$ because of valence angle restrictions, in this case the 120° meta linkages. Thus the projection of an effective "bond" l onto the axis of the fully extended chain will be $l\sin(\theta/2)$. This yields a value for the persistence length q of 2.8 nm, in very reasonable agreement with the experimental value of about 3 shown in Figure 7. In terms of the persistence length q, BPDA-PDA appears to be quite similar in flexibility to PMDA-ODA in the amic acid form.

Imidized Materials. The persistence length may also be estimated for the imidized form of BPDA-PDA. The imidized polymer may be represented as a chain of successive bonds of 1.26 and 0.43 nm, very similar to the all-meta isomer, except that the angle between successive virtual bonds is increased to 150° as shown in Figure 9. This increase has a dramatic effect on the calculated dimensions with the freely rotating model and leads to an estimated persistence length of 6 nm, double the estimated

q for the BPDA-PDA amic acid. In contrast, with PMDA-ODA, the calculated persistence length increases only about 50% from the amic acid to the imide form.[23] The BPDA-PDA polyimide appears insoluble in any known solvent, so this calculated value for q cannot be compared with an experimental value. However, the small increase in q for PMDA-ODA is consistent with measurements of the imidized polymer in sulfuric acid.[9] The q of 6 nm for BPDA-PDA polyimide is nearly twice the q of 3.1 nm for PMDA-ODA polyimide.[23] The difference in rigidity between the PMDA-ODA polyimide and the BPDA-PDA polyimide is reflected in the higher modulus and smaller elongation at break observed for BPDA-PDA.[26] The high softening temperature observed for these materials is more reflective of their intermolecular interactions in the solid state than of their inherent molecular rigidity.[23,27] In particular, the introduction of linkages that may be modeled as "kinks" in the backbone, such as the BPDA or ODA, appear to have little effect on the softening temperature.[27] In contrast, the introduction of these groups into an otherwise fully extended backbone has a dramatic effect on the molecular flexibility. It has been suggested that this is due to the ease with which the extended conformations of these chains can be packed together.[24,27] These values of q are far below the 50-nm range reported for "rodlike" polymers such as poly(phenyleneterephthalamide) or poly(hexyl isocyanate). However, polymers with similar values of q, such as poly(2,5-benzoxazole) with q reported as about 5 nm, are reported to exhibit liquid-crystalline textures at concentrations as low as 14%.[28] This is presumably due to the more extended conformations being favored energetically as the concentration is increased. Ordered structures observed in films of the imidized PMDA-ODA and BPDA-PDA are consistent with this.[29]

Conclusions

The results of the above work suggest classical step growth behavior for the polymerization of BPDA and PDA to the poly(amic acid) in both NMP and DMSO. The molecular weight of the poly(amic acid) can be controlled by offsetting the stoichiometry of the monomers. The dilute solution measurement of both light scattering and intrinsic viscosity can be affected by solvent purity in NMP. Caution should therefore be exercised when using one-point intrinsic viscosity measurements in predicting molecular weight of the poly(amic acids) in NMP due to the polyelectrolyte effect. The molecular parameters of BPDA-PDA, like PMDA-ODA, can be approximated by a freely rotating chain at high molecular weights while the equivalent wormlike chain is appropriate at lower molecular weight. The molecular parameters were used to calculate the persistence lengths of the wormlike chain model for BPDA-PDA and then compared to those of PMDA-ODA and its esters.

References and Notes

(1) Numata, S.; Oohara, S.; Imaizumi, J.; Kinjo, N. *Polym. J.* **1985**, *17*, 981.

(2) Numata, S.; Oohara, S.; Fujisaka, K.; Imaizumi, J.; Kinjo, N. *J. Appl. Polym. Sci.* **1986**, *31*, 101.

(3) Kochi, M.; Horigome, T.; Mita I.; Yokota, R. In *Recent Advances in Polyimide Science and Technology*; Weber, W. D., Gupta, M. R., Ed.; Mid-Hudson Section, Society of Plastics Engineers, Inc.: New York, 1987; pp 192–200.

(4) Kochi, M.; Uruji, R.; Iizuka, T.; Mita, I.; Yokota, R. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 441.

(5) Numata, S.; Fujisaki, K.; Kinjo, N. *Polymer* **1987**, *28*, 2282.

(6) Numata, S.; Fujisaka, K.; Makino, D.; Kinjo, N. In *Recent Advances in Polyimide Science and Technology*; Weber, W. D., Gupta, M. R., Ed.; Mid-Hudson Section, Society of Plastics Engineers, Inc.: New York, 1987; pp 164–173.

(7) Misawa, Y.; Kinjo, N.; Hirao, M.; Numata, S.; Momma, N. *IEEE Trans. Electron Devices* **1987**, *34*, 621.

(8) Volksen, W.; Cotts, P. In *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; Vol. 1, pp 163–170.

(9) Cotts, P. In *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; Vol. 1, pp 223–236.

(10) Cotts, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 923.

(11) Wallach, M. *J. Polym. Sci., A-2* **1967**, *5*, 653.

(12) Birshtein, T. M.; Zubkov, V. A.; Milevskaya, I. S.; Eskin, V. E.; Baranovskaya, I. A.; Koton, M. M.; Kudryavtzev, V. V.; Sklizkova, V. P. *Eur. Polym. J.* **1977**, *13*, 375.

(13) Kim, S. H.; Cotts, P. M. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 109.

(14) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(15) Miwa, T.; Numata, S. In *Polyimides: Materials, Chemistry and Characterization*; Feger, C., Khojasteh, M. M., McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989.

(16) Cotts, P. M. *Proc. ACS Div. Polym. Mater. Sci. Eng.* **1986**, *54*, 686.

(17) Walker, C. C. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1649.

(18) Nefedov, P. P. *Polym. Sci. USSR* **1981**, *23*(1), 1055.

(19) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.

(20) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.

(21) Cotts, P. M.; Volksen, W. *Polym. News* **1990**, *15*, 106.

(22) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.

(23) Birshtein, T. M. *Vysokomol. Soyed.* **1977**, *A19*, 54; *Polym. Sci. USSR* **1977**, *19*, 63.

(24) Tonelli, A. E. *Macromolecules* **1973**, *6*, 503.

(25) Erman, B.; Flory, P. J.; Hummel, J. P. *Macromolecules* **1980**, *13*, 487.

(26) Smith, T. L.; Kim, C. S. *Polym. Eng. Sci.* submitted for publication.

(27) Zubkov, V. A.; Birshtein, T. M.; Milevskaya, I. S. *Vysokomol. Soyed.* **1975**, *A17*(9), 1955; *Polym. Sci. USSR* **1975**, *17*, 2252.

(28) Chow, A. W.; Bitler, S. P.; Penwell, P. E.; Osborne, D. J.; Wolfe, J. F. *Macromolecules* **1989**, *22*, 3514.

(29) Takahashi, N.; Yoon, D. J.; Parrish, W. *Macromolecules* **1984**, *17*, 2583.